EFFECT OF HYDROGEN ADSORPTION TO THE HIGH STRENGTH STEEL IN SOIL AQUEOUS ENVIRONMENT

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ABSTRACT

This thesis is carried out to investigate the effect of hydrogen adsorption to the high strength steel in soil aqueous environment. This study is about how hydrogen adsorption in soil aqueous environment will affect the material appearance and loss of weight will be use to determine the the corrosion rate. This study is using three different concentration of H_2SO_4 to add in the soil; 2 ml, 4 ml and 6 ml and H_2O. Increasing H_2SO_4 concentration promoted higher corrosion rate and higher loss of weight. Under the tested condition it was found that the higher concentration of H_2SO_4 led to a higher corrosion rate and higher loss of weight. It is concluded that by increasing H_2SO_4 concentration leads to the increasing of corrosion rate.

ABSTRAK

Tesis ini dijalankan untuk mengkaji kesan hidrogen penjerapan untuk keluli kekuatan tinggi di dalam persekitaran berair tanah. Kajian ini adalah tentang bagaimana hidrogen penjerapan dalam persekitaran berair tanah akan menjejaskan penampilan material dan kehilangan berat badan akan digunakan untuk menentukan kadar hakisan. Kajian ini menggunakan tiga kepekatan berbeza H_2SO_4 untuk menambah di dalam tanah; 2 ml, 4 ml dan 6 ml dan H_2O. Meningkatkan H_2SO_4 kepekatan digalakkan kadar kakisan yang lebih tinggi dan kerugian yang lebih tinggi berat badan. Dalam keadaan yang diuji didapati bahawa kepekatan yang lebih tinggi H_2SO_4 membawa kepada kadar yang lebih tinggi hakisan dan kerugian yang lebih tinggi berat badan. Ini menunjukkan bahawa dengan meningkatkan kepekatan H_2SO_4 membawa kepada peningkatan kadar hakisan.

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LIST OF SYMBOLS

mm	Millimetre
ml	Millilitre
%	Percent
μm	Micrometre
^{o}	Degree
g	Gram
mm/y	Millimetre per year

LIST OF ABBREVIATIONS

H_2SO_4	Sulphuric Acid
SI	International System of Units
rpm	*Revolutions per Minute*
EDM	Electric Discharge Machining
H_2O	Water

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Nowadays, pipelines for gas and oil transportation are very significant component of national economic infrastructures as well as global. So, the huge plans for installation of new pipelines between continents need more attention to their reliable and safe exploitation. In this context, the hydrogen degradation of pipeline steels is the most important problem among other structural integrity problems from the reasons stated.

Firstly, pipelines steels encounter hydrogen during the transportation of sour crude oil and other petroleum products (Azevedo, 2007). Furthermore, free corrosion process is caused by external environmental conditions, where hydrogen can evaluate on metal surface as the result of cathodic counterpart of the anodic dissolution reaction (Cheng and Niu, 2007) (Dey et al, 2006). Hydrogen charging of pipeline steels is also possible under in-service condition when a cathodic protection system is in place (Dey et al, 2006)

The second reason is increases of attention to the problem hydrogen degradation of pipeline steels is the fact that hydrogen will play a decisive role in a future energy system, when fossil fuels have become limited, expensive and unsuitable from ecological reasons. For the given types of pipeline steels, there are some comparisons that can be made. For example, the factor of cathodic hydrogen charging, time of exposition and hydrogen concentration in metal.

1.2 OBJECTIVE OF STUDY

To investigate the effect of hydrogen adsorption to the high strength steel in soil aqueous environment.

1.3 SCOPE OF PROJECT

This project concentrated on how soil contains of different concentration of sulphuric acid affect hydrogen adsorption to the high strength steel and its corrosion rate. The scope of this project includes the preparation of material where the high strength steel was taken from laboratory and then machined to desired dimension. After preparation of 9 samples, 1 of the sample have been test by tensile test process to get strength of the material before exposure. After tensile test process has been done, the microstructure and hardness of the specimen were investigated. 8 more samples will be exposing in the soil environment with different concentration of sulphuric acid (H_2SO_4). Weight loss will be use to determine the corrosion rate of the samples.

1.4 PROBLEM STATEMENT

This study concern on the effect of hydrogen adsorption to the high strength steel in soil aqueous environment where soil sample will be add with different concentration of sulphuric acid. Sample will be exposed in soil environment which contain hydrogen from the water in the soil and different concentration of sulphuric acid for about 1 week.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter discusses the literatures that are related to the effect of hydrogen adsorption on the high strength steel. This chapter will review on the material that are used, the processes that are used for specimens preparation, the tensile test processes and the electrochemical test on the specimen.

2.2 THE METALLURGY OF STEEL

When a small amount of carbon is added to iron, thus steel is obtained. So, all steel have some carbon and iron in its mechanical properties and a little bit of alloying elements since the influence of carbon on mechanical properties of iron is much larger than other alloying elements. It also can be said that steel is a crystalline alloy of iron, carbon and several other elements. These alloys vary both in the way they are made and in the amount of the materials added to the iron.

2.2.1 Plain Carbon Steel

Carbon steel is one of the most used steel. The properties of carbon steel depend on the amount of carbon that contains in the steel. Most of the carbon steel has a carbon content of less than 1%. Carbon steel is also used in many products that are commonly used such as structural beams, car bodies, kitchen appliances, and cans. There are three types of carbon steel that are low carbon steel, medium carbon steel and high carbon steel and each one of them differs in the amount of carbon that it contains. So, plain carbon steel is a type of steel that contains the maximum carbon content of 1.5% along with small percentages of silica, sulphur, phosphorus and manganese.

Low carbon steel or mild steel is a carbon steel that contains carbon up to 0.25% and responds to heat treatment as improvement in the ductility of the steel is concerned but has no effect on its strength properties.

Medium carbon steel is a carbon steel that contains carbon ranging from 0.25% to 0.7% and it improves in the machinability by heat treatment. This steel is especially adaptable for machining or forging where surface hardness is desirable

High carbon steel is plain carbon steel that contains carbon ranging from 0.7% to 1.05% and it is especially classed as high carbon steel. It is very hard in heat treatment and it will withstand high shear and wear and will be subjected to little deformation. There are also other properties of plain carbon steel that needs to be considered as shown in table 2.1.

Table 2.1: Properties of low carbon steel

Material	Density ($\times 10^3 kgm^{-3}$)	Thermal conductivity ($Jm^{-1}K^{-1}s^{-1}$)	Thermal expansion ($\times 10^{-6}K^{-1}$)	Young's modulus (GNm^{-2})	Tensile strength (MNm^{-2})
0.2% C Steel	7.86	50	11.7	210	350
0.4% C Steel	7.85	48	11.3	210	600
0.8% C Steel	7.84	46	10.8	210	800

Source: Raghavan (2001)

The atomic diameter of carbon is less than the interstices between iron atoms and so the carbon goes into solid solution of iron. As carbon dissolves in the gabs between the atoms, it distorts the original crystal lattice of iron. This change of crystal lattice of interferes with the external applied strain to the crystal lattice by mechanically blocking the dislocation of crystal lattices and the steel is now having higher mechanical strength. The more carbon added to the solid solution of iron, the more distortion it will made to the crystal lattice and thus the mechanical strength is increasing. Thus the high carbon steel has more carbon in the mechanical properties and low carbon steel has small amount of carbon in its mechanical properties. But by adding the carbon into iron, there are other properties that are influenced by the carbon that is the ductility which is the ability of iron to undergo plastic deformation. Thus, the more carbon added to the iron, the strength is increasing but the ductility is reduced. Adding carbon is not the only way to increase the strength of steel. More carbon amount means that when in welding process, it will cause trouble because of the strength. Figure 2.1 shows diagram of temperature versus weight % of carbon of carbon steel.

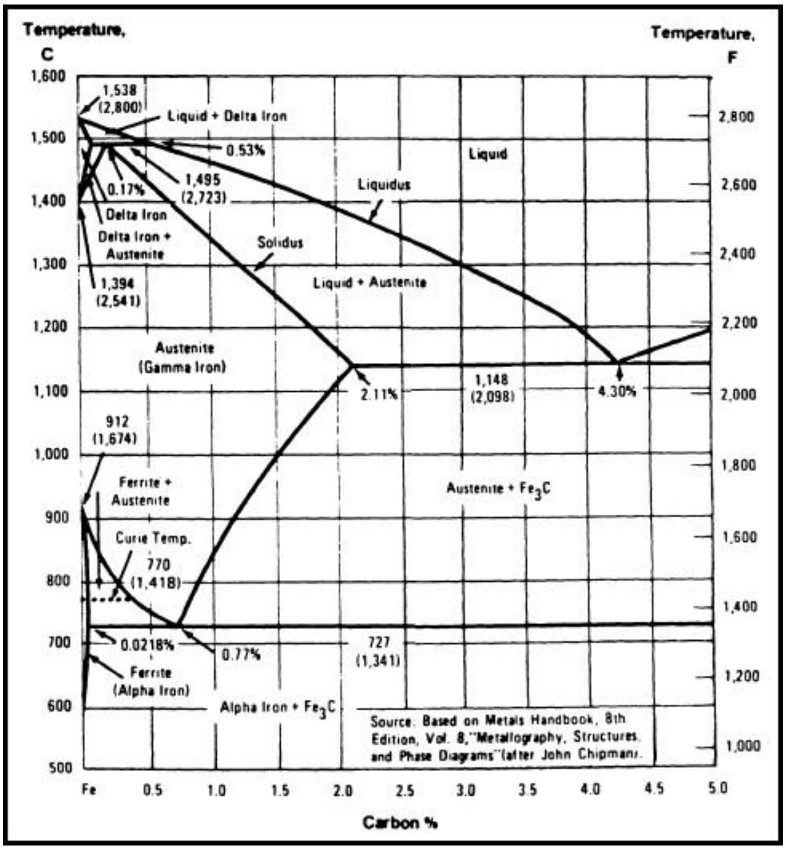

Figure 2.1: Temperature versus weight % of carbon of carbon steel

Source: Kumar

Ferrite (α) is virtually pure iron with body centered cubic crystal structure (BCC). It is stable at all temperatures up to 9100°C. The carbon solubility in ferrite depends on the temperature where the maximum carbon amount is 0.02% at 723°C. Cementite is an Iron Carbide (Fe_3C), a compound iron containing 6.67% of carbon by weight. It is commonly used as a tool in lathe machine for machining the material. Pearlite is a fine mixture of ferrite and cementite arranged in lamellar form. It is stable at all temperatures below 723°C. Austenite (γ) is a face centered cubic structure (FCC). It is stable at temperatures above 723°C depending on the carbon content. It can dissolve up to 2% of carbon.

The maximum solubility of carbon in the form of Fe_3C in iron is 6.67%. If the addition is above the limit, it will result in formation of free carbon or graphite in iron. At 6.67% of carbon, iron transforms completely into cementite of Fe_3C that is Iron Carbide. Generally, carbon content in structural steels is in the range of 0.12-0.25%. Up to 2% of carbon, we will get a structure of ferrite + pearlite or pearlite + cementite depending on the whether the carbon content is less than 0.8% or beyond 0.8%. Beyond 2% carbon in iron a brittle cast iron is formed.

Furthermore, the hardness, brittleness and ductility are very important properties as they determine mainly the way these different carbon content steels are used. Considering the microstructure of slowly cooled steel for example mild steel with 0.2% carbon. Such steel consists of about 75% of proeutectoid ferrite that forms above the eutectoid temperature and about 25% of pearlite with pearlite and ferrite being microstructure components of steel. When the carbon content in steel is increased, the amount of pearlite increases until we get the fully pearlitic structure of a composition of 0.8% carbon. Beyond 0.8%, high carbon steel contain proeutectoid cementite n addition to pearlite.

But in slowly cooled carbon steels, the overall hardness and ductility of the steel are determined by the relative proportions of soft, ductile ferrite and the hard, brittle cementite. The cementite content increases with increasing carbon content, resulting in an increase of hardness and the decrease of ductility, as we go from low to high carbon steels.

There are also some limitations if carbon steels that are it there can't be strengthening beyond 100000 psi without significant loss in toughness (impact resistance) and ductility. Then, the large sections cannot be made with martensite structure throughout, and thus are not deep hardenable. Rapid quench rates are necessary for full hardening in medium-carbon leads to shape distortion and cracking of heat treated steels.

The characteristic of plain-carbon steels is that it has poor impact resistance at low temperatures. It also has a poor corrosion resistance for engineering problems. That means that it is easily corroded when the corroding element exists and it also oxidise readily at elevated temperature. Figure 2.2 shows three types of plain carbon steel microstructure.

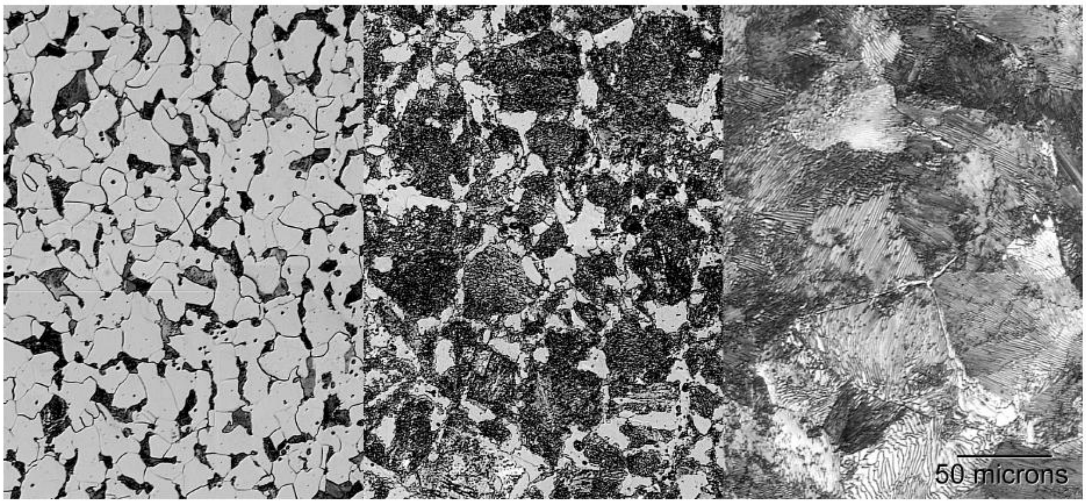

Figure 2.2: Three plain carbon steels, from left to right: 1018, 1045 and 1095. Increasing the carbon content (from 0.18% to 0.95%) causes the amount of ferrite (light) to decrease and the amount of pearlite (dark, lamellar) to increase.

Source: Meier (2004)

2.3 CORROSION OF STEEL

Corrosion of steel is an electrochemical reaction followed by a chemical reaction:

Anodic reaction (Bayliss, D.A and Deacon, D.H.1985):

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{2.1}$$

The corrosion reactions can be illustrated using chemical terminology as follow equation (2.1). This is simple way of describing the process where iron is removed as charged particle called ions (Fe^{2+}) and electron (e-) carry current to balance the electric charge. Clearly a balancing reaction must occur at the cathode and under ordinary natural exposure conditions this can be represented as follows:
Cathodic reaction:

$$\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{2.2}$$

In short, hydroxyl ions are produced at the cathode. These two reactions can be combined in a chemical equation (2.3):

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow 2OH^{-} + Fe^{2+} \tag{2.3}$$

The ferrous and hydroxyl ions react together to form ferrous hydroxide:

$$2OH^{-} + Fe^{2+} \rightarrow Fe(OH)_2 \tag{2.4}$$

This is simple form of rust which unstable and is eventually oxidized (i.e. react with oxygen) to form the familiar reddish brown rust, chemically denoted FeOOH. This is the form of rust usually produced in air, natural water and soils. However, under acidic conditions hydrogen is produced at the cathode and the corrosion product may be Fe_3O_4 (magnetite).

2.4 HYDROGEN EMBRITTLEMENT

At elevated temperatures and significant hydrogen partial pressures, hydrogen will penetrate carbon steel, reacting with the carbon in the steel to form methane. The pressure generated causes a decrease of the toughness or ductility of a metal due to the presence of atomic hydrogen (hydrogen embrittlement) and failure by cracking or blistering of the steel. The removal of the carbon from the steel (decarburization) results in decreased strength.

The embrittlement of metal or alloy by atomic hydrogen involves the ingress of hydrogen into a component, an event that can seriously reduce the ductility and load-bearing capacity, cause cracking and catastrophic brittle failures at stresses below the yield stress of susceptible materials.

Hydrogen embrittlement has been recognized classically as being of two types. The first one is known as internal hydrogen embrittlement, occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification. While the second type, environmental hydrogen embrittlement, results from hydrogen being absorbed by solid metals. This can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection, and operating in high-pressure hydrogen.

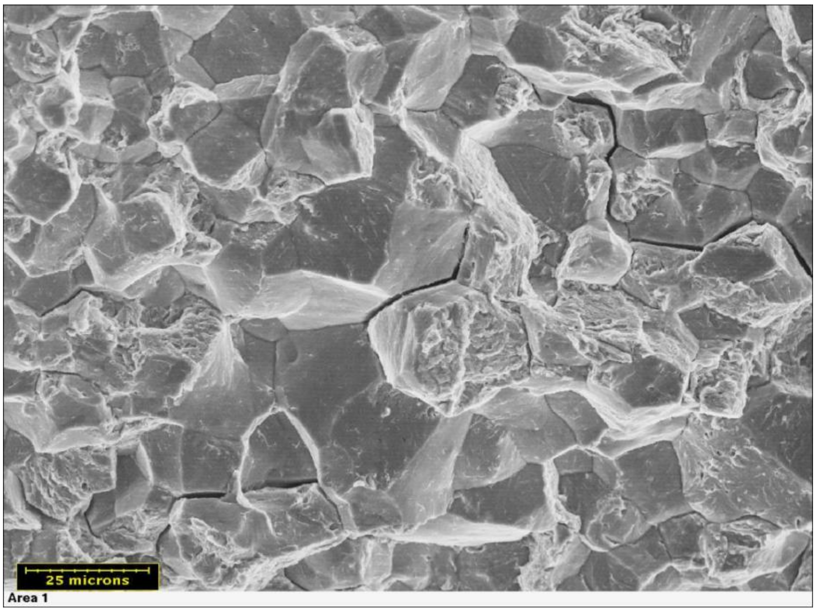

Figure 2.3: Hydrogen Embrittlement

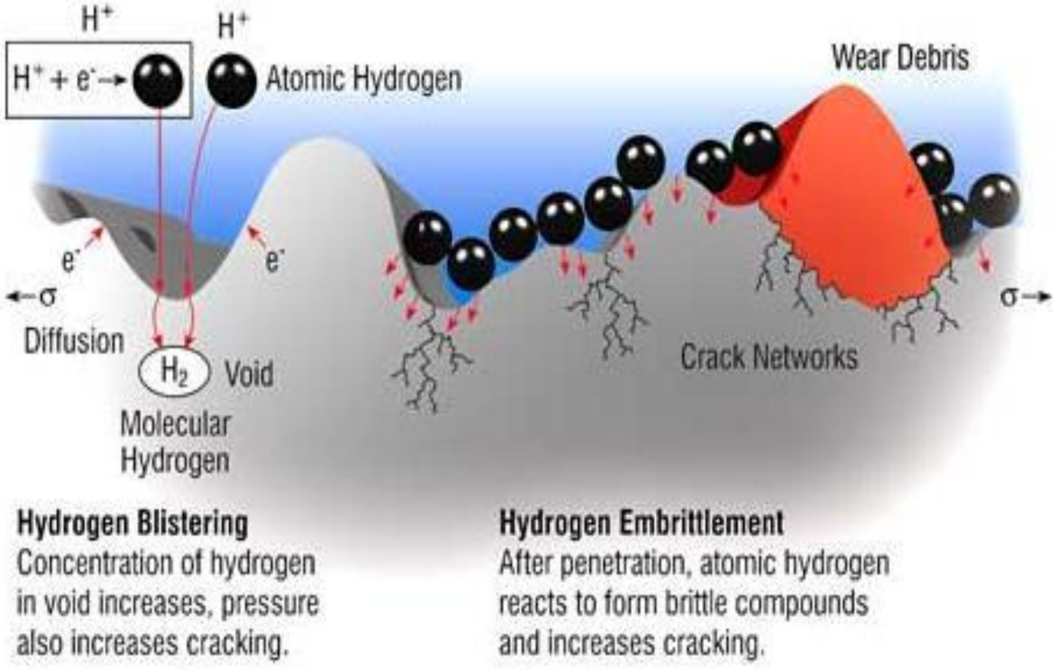

Figure 2.4: Hydrogen-induced Embrittlement and Blistering Caused by Water Contamination

Source: Callister, W. D. (2007)

2.5 MECHANISM OF HYDROGEN ENTRY INTO METALS

Hydrogen entry into metals or alloys may result in degradation of mechanical properties (Lowis and Aladjem, 1996). Hydrogen can be introduced into metals and alloys in certain environments and there are numerous ways for hydrogen to enter metals. Among these are exposure to hydrogen gas and electrolytic deposition of hydrogen on metal electrodes. The electrolytic process is a very effective way of introducing hydrogen since it can sustain high equivalent pressure of hydrogen gas at metal surface. Hydrogen entities are initially contained in interstitial sites of metal lattices as monatomic state.

For gas phase, initial studies of the solubility of hydrogen in iron and other metals can be attributed to (Sieverts et al, 1911) who found experimentally that amounts of hydrogen dissolved in metal can be directly proportional to the square root of the hydrogen pressure, Hydrogen dissolved in metal can be directly proportional to the square root of the hydrogen pressure, $P_{H_2}^{1/2}$ (atm$^{1/2}$), and the equilibrium can be written as

$$1/2H_{2(g)} + M = MH_{(abs)} \tag{2.5}$$

Thus the solubility of hydrogen, C, in metal is

$$C = K\,P_{H_2}^{1/2} \tag{2.6}$$

The solubility of hydrogen in iron can be represented as a function of temperature by an equation such as

$$C(ppm) = 42.7P_{H_2}^{1/2}\,\mathrm{exp}(-\frac{3280}{T}) \tag{2.7}$$

In the case of hydrogen entry into metal in aqueous solution, (Devanathan et al, 1966) (Latanision and Kurkela, 1983) (Iyer et al, 1990) have found that amounts of dissolved hydrogen in iron can be directly proportional to the square root of the cathodic charging current density, $i^{1/2}$ (Amp/m^2)$^{1/2}$. The mechanism involves coupled discharge-chemical absorption. The overall reaction sequence can be summarized as

$$H^{+} + e^{-} + M \xrightarrow{k1} MH_{(ads)} \underset{k_{-3}}{\overset{k3}{\rightleftharpoons}} MH_{(abs)}$$

$$\downarrow$$

$$+MH_{(ads)} \rightarrow 2MH_{(ads)} \xrightarrow{k2} H_2 + M \qquad (2.8)$$

An equation analogous to Eq. 2 can be expressed by

$$C = Ki^{1/2} \qquad (2.9)$$

The solubility of hydrogen in iron at 25 °C from 1M H_2SO_4 solution has been reported (Wu and Int, 1992) as

$$C(ppm) = 0.017i^{1/2} \qquad (2.10)$$

2.6 HYDROGEN ADSORPTION

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface.

In deoxygenated, near-neutral pH solution, hydrogen atoms are generated on the steel surface by the electrochemical reduction of water molecules (Cheng and Niu, 2007):

$$H_2O + e \rightarrow H_{ads} + OH^{-} \qquad (2.11)$$

The adsorbed hydrogen atoms can subsequently combined to H_2 molecules by the chemical reaction:

$$2H_{ads} \rightarrow H_2 \tag{2.12}$$

Or the electrochemical reaction:

$$H_{ads} + H_2O + e \rightarrow H_2 + OH^- \tag{2.13}$$

Or can be absorbed by the steel:

$$H_{ads} \rightarrow H_{abs} \tag{2.14}$$

The absorbed hydrogen atom concentration under the cathodic polarization depends on the hydrogen atom recombination mechanisms. When the chemical reaction (2.12) dominates the hydrogen atom recombination, the applied cathodic polarization enhances the generation of hydrogen atoms and thus the amount of hydrogen atoms penetrating into the steel. The absorbed atom concentration will increase continuously with the cathodic polarization potential. In the case of electrochemical reaction (2.13) dominating the hydrogen atom recombination, the cathodic polarization promotes the generation of hydrogen atoms through reaction (1), and simultaneously, enhances the hydrogen atom recombination through reaction (3). Thus, the role of cathodic polarization is to generate hydrogen atoms and also to recombine hydrogen atoms.